# **CHAPTER 19**

# NONRADIOLOGICAL MONITORING

#### **ABSTRACT**

This chapter summarizes available nonradiological monitoring data. Based on these data, there is little evidence to suggest that Savannah River Site (SRS) operations have resulted in elevated <u>concentrations</u> of nonradiological contaminants at locations beyond the Site boundary. This is true for all identified chemicals and heavy metals of concern measured in surface water, groundwater, and ambient air.

## INTRODUCTION

We conducted a study to identify available nonradiological monitoring data and evaluate its potential for supporting <u>dose reconstruction</u>. A thorough evaluation of nonradiological contaminant (e.g., chemicals, heavy metals, and pesticides) monitoring is limited by the amount of data available for analysis. More information is available about <u>radionuclides</u> released from the SRS than environmental and <u>effluent monitoring</u> data for nonradiological contaminants. Consequently, conclusions inferred from available nonradiological data are inherently less certain than those based on radiological data.

Environmental information documents developed for environmental impact statements for waste sites are one source of information for characterizing past practices and evaluating their potential impact on current contamination. Other sources of information about the current status of onsite contamination are the Resource Conservation and Recovery Act (RCRA) and Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) projects currently in progress at the SRS. These projects are primarily evaluating present and potential future releases, but the information can also be used to investigate past activities and releases at the Site. Research studies and monitoring conducted to support environmental compliance activities may be especially useful for persistent chemical materials that were not routinely monitored before the compliance regulations or cleanup agreements were established. For the purpose of reconstructing chemical releases, recent monitoring data for RCRA or CERCLA characterization studies may be the best and sometimes only information available.

# AVAILABLE MONITORING DATA

Environmental and effluent monitoring for nonradiological materials was not conducted during the early years of operation at the SRS. Most of these monitoring programs were developed in the 1980s. Industrial hygiene measurements for nonradiological compounds in work areas were also very limited before the late 1970s.

Monitoring for nonradiological materials in liquid <u>effluents</u>, streams, groundwater, drinking water, the Savannah River, air, fish, and wildlife was expanded over the years. However, most of the expansion occurred after 1980, and most of this growth was in onsite groundwater sampling. The streams and Savannah River were sampled monthly or quarterly for metals, chlorides, and water quality. Sediments were sampled annually after 1980 (<u>Davis et al.</u> 1989). Beginning in the

late 1980s, ambient air was generally sampled continuously for sulfur dioxide, nitrogen oxides, and ozone. Quarterly monitoring of nonradioactive parameters in wastewater effluent began in 1982 to demonstrate compliance with RCRA and South Carolina Hazardous Waste Regulations. In 1983, many parameters were reduced to an annual monitoring schedule.

Concentrations were often not detectable for nonradiological contaminants, or there was no apparent Site influence on concentrations in the Savannah River, ambient air, or offsite soil. For most of these materials, monitoring data are likely to be of marginal or no use for dose reconstruction. Because existing chemical monitoring data are severely limited and these data were used to estimate source terms for chemicals, a detailed description of the data is not provided here (see Chapters 17 and 18 for a discussion of available chemical monitoring data). We reviewed data for nitrates in surface water and other metals in coal and ash basin and pile runoff. We evaluated these data as supporting evidence for source term estimates and present the data in the source term sections of this report, which detail chemicals released to air and water. Chapter 20 discusses data regarding mercury and chromium concentrations in groundwater, surface water, sediments, and fish. The following sections summarize available surface water quality, groundwater quality, and ambient air monitoring data that have been collected at locations on or in the vicinity of the SRS.

## SURFACE WATER QUALITY MONITORING

<u>Chapter 5</u> describes the surface water affected by the Site, potential contaminant flow to surface waters, and the National Pollutant Discharge Elimination System (NPDES) outfalls. The surface water bodies that flow to the Savannah River are of concern for dose reconstruction. Examples of plant discharges to surface water flowing to the river include Pen Branch, which received heat exchanger <u>cooling water</u> from K-Area and flow from Indian Grave Branch; K-Reactor retention basin, which <u>outcropped</u> into Indian Grave Branch and flows into Pen Branch; Steel Creek, which receives contaminants migrating from the P-Area <u>seepage basins</u>; L-Lake, which enters Steel Creek; and F-Area and H-Area seepage basins, which outcrop groundwater to Four Mile Creek.

The Academy of Natural Sciences of Philadelphia, under contract to Du Pont, has performed independent surveys of water quality since 1951. The program, which included diatom diversity studies and other monitoring, was established at plant startup and was directed for many years by Dr. Ruth Patrick, Curator of Limnology.

The SRS began a routine monitoring program to evaluate the chemical quality of Savannah River water upriver and downriver of the Site in October 1959. Water was collected continuously at an upriver location (R-2) and at the U.S. Highway 301 bridge crossing (R-10) (refer to Chapter 13 for figure showing sampler locations). Samples were analyzed weekly for color, pH, alkalinity, hardness, conductivity, total dissolved solids, dissolved oxygen, sulfide, sulfate, total iron, chloride, nitrate, nitrite, biological oxygen demand, lignin, and surfactant (Zeigler et al. 1986). Following the first year of the program, Van Wyck (1960) concluded that SRS operations did not affect the water quality of the river.

Savannah River water quality monitoring data are reported in monthly and annual reports from 1972 (Du Pont 1973) to the present. The annual reports compare the water quality analysis results to the South Carolina standards for a Class B stream. Class B streams are defined as "freshwaters suitable for secondary contact recreation and as a source for drinking water supply

after conventional treatment in accordance with requirements of the SCDHEC; suitable for fishing, survival and propagation of fish, and other fauna and flora; suitable also for industrial and agricultural uses" (Mikol et al. 1988). For example, the 1985 and 1986 annual reports summarize the water quality program results by stating that, except for temperature in Pen Branch, all stream analyses were within South Carolina standards for a Class B stream, and, except for fecal coliform, there was no difference in water quality above and below the Site (Zeigler et al. 1986, 1987).

By 1988, continuous paddlewheel samplers were used to sample river and stream water for many water quality parameters and chemicals, including heavy metals. Methods of analysis were based on U.S. Environmental Protection Agency (EPA) guidelines and subsequent guidance, which are provided by Cummins et al. (1991).

<u>Table 19-1</u> summarizes data collected during a 3-month period in 1959. The results indicated that water quality parameters measured downriver were not significantly different from those measured upriver, and that the plant had not adversely affected the water quality as measured by these parameters (<u>Van Wyck</u> 1960).

Table 19-1. Savannah River Water Quality Data Measured in 1959 Above and Below the SRS (mg L<sup>-1</sup> [ppm])

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Water	Upstream			Downstream		
quality	$(\text{mg } L^{-1})$			$(\text{mg L}^{-1})$		
parameter	Maximum	Minimum	Average	Maximum	Minimum	Average
Chloride	3.20	0.87	1.72	3.50	0.97	1.68
Nitrate	0.02	0.01	0.01	0.02	0.01	0.01
Sulfate	5.60	0.02	1.21	4.20	0.02	1.13
Nitrite	0.004	0.001	0.002	0.003	0.002	0.002
Surfactants	0.08	0.01	0.03	0.22	0.01	0.03

Although nitrate concentrations averaged 0.01 mg  $L^{-1}$  in 1959, Savannah River water quality measurements during January through June from 1960 to 1967 indicated that nitrates upriver and downriver of the plant averaged about 0.30 mg  $L^{-1}$ . However, there was generally little difference between upriver and downriver concentrations during this time period. The maximum nitrate value reported was 1.81 mg  $L^{-1}$  (Du Pont 1967).

Aperture cards (handwritten compilations of original environmental monitoring results that were photographed in a format similar to microfiche) detailing Savannah River water quality data were located for Savannah River sampling stations R-2 and R-10 for 1960, 1961, 1962, 1963, and 1964. Water quality data for Lower Three Runs Creek for 1960, 1961, 1962, 1963, and January to September of 1964 were also located. These data are generally consistent with the data reported in the various Site reports. For example, the 1961 handwritten data appear to match the more legible summary data in the December monthly report (Du Pont 1961).

Most of the water quality parameters measured before 1973 are not specific for chemicals of concern for this study. We reviewed monitoring results for nitrates and heavy metals, the only analytes selected as chemicals of concern, for the Savannah River and Four Mile Creek. Chapter 18 summarizes nitrate discharges to Four Mile Creek from the separations areas. Chapter 20 evaluates mercury and chromium environmental monitoring results and Chapter 18 characterizes mercury releases.

In 1973, a summary report stated that monitoring for nonradioactive materials in Savannah River water was conducted periodically near Jackson, South Carolina, and monthly grab samples were taken below the plant at the U.S. Highway 301 bridge (R-10). Concentrations at these two sites were compared through the 1960s and 1970s, and there were no significant differences in the concentrations of nitrate, mercury, sulfate, and metals above and below the plant (Reinig et al. 1973). In 1973, concentrations of sulfide and chloride appear to be greater above than below the SRS (Du Pont 1974). The chloride concentrations in Savannah River water had increased both above and below the plant in 1982. The increase was attributed to offsite upriver industrial sources (Du Pont 1983).

In June 1973, routine water quality monitoring was expanded to include carbonate, ammonium, sulfate, phosphorus, calcium, total iron, sodium, mercury, and aluminum. Mercury monitoring in river and stream sediments was also initiated in the early 1970s (Arnett 1993). With the exception of fecal coliform and temperature, water quality standards were not exceeded for any of the onsite streams or the Savannah River.

In 1979, the monthly Works Technical Report gave estimates of the concentration of water quality parameters in the Savannah River. Estimates of contaminant transport (in kilograms) were made for each month and year-to-date based on the concentrations (Du Pont 1979a). The average, maximum, and minimum concentrations; the calculated transport for the month of December; and the totals for 1978 were given for nitrite, nitrate, sulfate, chloride, as well as several other water quality parameters. Values were given for location R-2 above the plant, location R-10 below the plant, and nine onsite stream locations. Lead levels were less than the detection limit, except the maximum concentrations measured in Tim's Branch at Road C (0.5 mg L<sup>-1</sup>). Iron and aluminum were also included, but no information for the other toxic metals of concern for this study was provided (Du Pont 1979a). Chapter 18 summarizes the 1978 year-to-date transport for nitrates measured in kilograms.

Since 1983, discharges from five ash settling basins in various areas around the SRS and their receiving streams were monitored monthly for pH and five metals and biweekly for suspended solids, oil, and grease. Monthly flow measurements were also made (Zeigler et al. 1985). Suspended solids exceeded the limit once from the H-Area ash basin in 1983 (Cummins et al. 1991).

In 1985, the South Carolina Department of Health and Environmental Control (SCDHEC) required a program to evaluate the quality of stormwater runoff. It required sampling of runoff from 17 industrial outfalls to SRS streams and six waste disposal sites during three separate rain events of 1 inch or more. The data were being evaluated at the time of the annual report, but preliminary data indicated no significant discharges of pollutants from any of the monitored outfalls (Zeigler et al. 1986).

In 1986, the concentrations of chemicals in surface water were regulated by SCDHEC under the NPDES. The NPDES monitoring data were reported in annual reports after 1986 and included outfall concentrations of chlorinated solvents, metals, phosphate, nitrate, sulfide, oil, and grease. Seventy outfalls were monitored in 1986, and 99.4% of all results were reported to have been within permit limits (Zeigler et al. 1987). Sixty-eight NPDES outfalls were monitored in 1987 with similar conclusions reported. In 1989, NPDES noncompliances (exceedance of discharge limits) were found for trichloroethylene from A-Area and for benzene from TNX Area. The Site reported that the source of these contaminants in the outfall effluent was unknown (Cummins et al. 1990). By 1990, surface water was monitored for nonradioactive contaminants at 76 effluent

outfalls from facilities at the SRS. Surface water was also monitored at locations along six onsite streams and at three locations on the Savannah River. After 1992, the annual environmental reports list the NPDES outfall locations and only detail releases that exceed discharge limits. Most often, the exceedance was for oil and grease, which were noted as sheen or another qualitative description (Arnett 1993). Westinghouse (1996) provides a detailed description of recent monitoring in the Savannah River watershed.

More recently, river sediments have been sampled by the Site and/or SCDHEC. Benzene, cadmium, carbon tetrachloride, pesticides, chrysene, manganese, mercury, polychlorinated biphenyls (PCBs), tetrachloroethylene, and toluene were all at levels below detection limits. The mean concentrations for the individual metals detected downstream were 0.016 mg kg<sup>-1</sup> for chromium, 0.02 mg kg<sup>-1</sup> for lead, 1.6 mg kg<sup>-1</sup> for magnesium, 2.6 mg kg<sup>-1</sup> for manganese, 0.028 mg kg<sup>-1</sup> for nickel, 10 mg kg<sup>-1</sup> for uranium, and 0.21 mg kg<sup>-1</sup> for zinc. These concentrations were less than the screening level, risk-based concentrations derived from EPA values by the Site, including uranium with a screening level of 45 mg kg<sup>-1</sup> (Westinghouse 1996). Comparisons of concentrations above and below the Site do not suggest that these pollutants originate at the Site. In general, the results of grab sample analysis in the annual reports for chemicals and metals are reported as being within the ranges observed in previous years.

Nonradiological contaminants, including nitrates, mercury, chromium, cadmium, lead, nickel, manganese, zinc, magnesium, arsenic, hydrogen sulfide, uranium, sodium hydroxide, detergents, and oil, have been discharged to surface waters in measurable amounts. <a href="#">Chapter 18</a> characterizes these releases. However, the transport of nonradiological contaminants offsite in concentrations that would present a hazard has not been demonstrated by environmental monitoring.

## GROUNDWATER QUALITY MONITORING

Recent monitoring of onsite groundwater has been extensive; however, it is not relevant to past releases because groundwater exposure pathways to the public are not now, and have not in the past been, complete. Groundwater flowing beneath the waste sites or seepage basins from which chemicals are being leached generally does not flow offsite. Based on evidence from tritium migration to surface water, there are three exceptions: (1) groundwater beneath the H-Area and F-Area Seepage Basins flows into Four Mile Creek, (2) groundwater beneath the K-Reactor retention basin flows into Indian Grave Branch, which flows into Pen Branch, and (3) groundwater beneath the P-Area seepage basins, which flows into Steel Creek.

Extensive groundwater sampling and analysis has been conducted since the mid-1980s. Much of this information has been collected to support characterization and cleanup activities. Improvements were made to groundwater sampling and sampling preservation techniques in 1983, including better flushing of wells before sampling and filtering of samples for metal analysis (Zeigler et al. 1985).

Unfortunately, the majority of the groundwater data are not useful for dose reconstruction because the groundwater contaminants have not traveled offsite. However, understanding which materials were discharged into an area may help evaluate which materials potentially migrated beyond these discharge areas. For example, measurable concentrations of volatile contaminants under waste sites and seepage basins suggest that these compounds might also have evaporated into the air after being discharged. Groundwater monitoring below waste disposal sites and

seepage basins has been used to identify potential contaminants of concern for remediation work. Summaries of contaminants identified in groundwater are provided in monthly, quarterly, and annual reports. Suspected contaminants were defined as materials that may have been introduced into the groundwater by the SRS facility, identified as such by statistical comparison of upgradient and downgradient water quality parameters. <u>Table 19-2</u> presents examples of this information.

Table 19-2. Chemicals Identified as Potential Contaminants Introduced to Groundwater as a Result of SRS Activities

		Annual Report
Location	Location Chemical Contaminants of Concern	
F-Area	a Cadmium, copper, manganese, iron, lead, sodium, nickel,	
Seepage Basin	zinc, fluoride, nitrate, foaming agents, and phenol	
	Acid, cadmium, copper, manganese, iron, lead, sodium,	1984
	nickel, zinc, fluoride, nitrate, radium, foaming agents,	
	phenol	
	Acid, sodium, nitrate	1985
	Acid, sodium, nitrate, cadmium, chromium, lead	1986
	Nitrates, lead, and sulfate. Also detected arsenic, cadmium,	1989
	chromium, mercury, selenium and fluoride and chlorinated	
	organics	
H-Area	Acid, chloride, mercury, manganese, iron, sodium, nitrate	1983
Seepage basin		
	Acid, chloride, iron, mercury, manganese, sodium, and	1984
	nitrate	
	Acid, mercury, sodium, nitrate	1985
	Acid, mercury, sodium, nitrate, lead	1986
M-Area	Acid, radium, chloride, iron, mercury, manganese, sodium,	1983
Seepage basin	and nitrate	
	Chloride, organic, cadmium, copper, manganese, nickel,	1984
	nitrate, and phenol	
	Organics, nitrate and sodium	1985
	Nitrate, lead, endrin, trichloroethylene, tetrachloroethylene,	1986
	carbon tetrachloride, sodium	

The M-Area seepage basin was taken out of service in 1985 (Zeigler et al. 1986). Galvanized well casings are thought to have contributed to apparent groundwater contamination by zinc, cadmium, lead, and iron. These casings were replaced with polyvinyl chloride (PVC) in 1985. The Site then reduced the number of contaminants monitored in groundwater in the vicinity of the seepage basins to include only acid, sodium, nitrate, mercury, and organics.

In a 1987 assessment of chemical constituents and estimation of inventories for SRP waste sites, <u>Looney et al.</u> (1987) selected chemicals of concern for each of the waste sites. Cadmium, chromium, lead, mercury, and nitrates were chemicals of concern identified at the Old F-Area Seepage Basin and F-Area and H-Area Seepage Basins. Total organic halogens were also listed for the Old F-Area basin. No contaminants of concern were identified for the Reactor Area seepage basins.

Groundwater near the D-Area had elevated levels of arsenic, cadmium, chromium, fluoride, mercury, lead, and selenium in 1989. Sulfate and chromium were high, exceeding the drinking

water standards by 600 and 55 times, respectively. Trichloroethylene and tetrachloroethylene were also above standards in groundwater below H-Area. The maximum concentration of mercury under the H-Area seepage basins exceeded the drinking water standards by nine times and was the highest level monitored at the SRS. Wells below the K-Area disassembly basin had elevated levels of lead, trichloroethylene, and tetrachloroethylene. No chemical constituents were detected above the drinking water standards at the K-area Reactor Seepage Basin. (Cummins et al. 1990).

Lead, trichloroethylene, and tetrachloroethylene were the most common nonradiological contaminants exceeding standards in monitoring wells onsite during 1992. Cadmium, chromium, lead, mercury, nitrate, and sulfate were greater than the drinking water standards in some wells (Arnett 1993).

## AMBIENT AIR MONITORING

Section 110 of the Clean Air Act Amendments of 1970 required each state to establish a network to monitor ambient air quality. In response to a concern about sulfur dioxide releases from the 400-D-Area, three ambient air monitors were located in a straight line from the 400-D-Area to 200-F-Area in 1973. The monitor situated midway between D-Area and F-Area was located on the Cassel's Fire tower (Peterson 1973). By 1976, both South Carolina and Georgia had implemented sampling networks. More extensive monitoring of ambient air quality was initiated at the SRS in 1977 (Zeigler et al. 1987). For example, a program to measure hydrogen sulfide and sulfur dioxide using monitoring equipment in mobile trailers began in 1977. Both were detected in ambient air most frequently at stations near D-Area. The maximum sulfur dioxide concentration was 190 ppb, and the average at all stations was about 4 ppb, well within the air quality standards established by Georgia and South Carolina (Du Pont 1979b). By the late 1980s, ambient air on and around the SRS was sampled continuously for sulfur dioxide, nitrogen oxides, and ozone.

After 1977, air quality data were summarized in tables in the annual environmental reports. Control of total suspended particulates and oxides of nitrogen was assessed by using opacity meters in the powerhouse stacks. Beginning in 1987, compliance with standards was also determined through tests conducted every 2 years by air emissions specialists under contract to the SRS. Although original documentation for most of these tests has not been found, the results of the test were located in Air Emission Inventory and Operating Permit Application supporting documents and files assembled in the early 1990s.

Occasionally, high opacity values in the 291-F stack were measured. The acid absorption column for F-Area separations process stack was renovated in 1986, after which the opacity requirement was met (Zeigler et al. 1987).

Since 1982, Georgia and South Carolina have operated ambient air quality monitoring stations for particulates, lead, ozone, nitrogen oxides, carbon monoxide, and sulfur dioxide near the SRP. Four to six monitoring stations have been operated onsite by private contractors. The air quality measurements onsite have been below the air quality standards, with the exception of ozone, which has been reported at concentrations greater than the standard at several locations.

Zeigler et al. (1986) reported that concentrations of ozone were higher than the annual standard of 120 ppb on 1 day in each of the years 1982, 1983, and 1985. Exceedance of the standard for 1 day each year is allowed by State regulations; consequently, the ambient air

concentrations were all reported as being within the standards. The high concentrations have generally been recorded in the summer months. Ozone concentrations were also reported to be high at offsite monitoring stations at the same time. Some reports attributed the elevated ozone concentrations to photochemical reactions of hydrocarbons and nitrogen oxides. In an environmental survey, <u>DOE</u> (1987) stated that "high concentrations of ozone may be due to volatile hydrocarbons such as those released from the air stripper in M-Area, the laboratories, <u>fuel</u> storage facilities and vehicles." However, elevated ozone concentrations were recorded in 1982 and 1983 before the air stripper was in use. In 1982, ozone concentrations above the standard were measured when the performance of the detection instrument was said to have been erratic, and the annual report states that "it is not known if the ozone level was actually above the 120 ppb standard" (<u>Zeigler et al.</u> 1985).

The annual environmental reports for 1984, 1985, and 1986 state that audits of the ambient air monitoring stations were performed quarterly. The calibration of the equipment was also evaluated quarterly (Zeigler et al. 1985, 1986)

By 1985, the SRS monitored air quality at five or six stations and the states of Georgia and South Carolina monitored air quality at eight stations near the SRS. The stations continuously measured total suspended particulate, sulfur dioxide, oxides of nitrogen, and ozone (Zeigler et al. 1987).

The annual and quarterly or special reports summarizing the data generally maintain that concentrations were within standards. For example, the 1986 annual report listed the state standards compared to the maximum concentration found at any of the SRS monitors for sulfur dioxide (Table 19-3).

In 1986, the annual ambient air concentrations for sulfur dioxide, compiled quarterly at four locations, averaged 2 ppb and ranged from 1 to 4 ppb. Nitrogen dioxide levels, measured at five locations, ranged from 0 to 9.6 ppb and averaged 4.32 ppb (Zeigler et al. 1987). In 1987, annual sulfur dioxide levels ranged from 1 to 6 ppb and averaged 3.2 ppb, while annual nitrogen dioxide levels ranged from 0 to 7 ppb and averaged 2.7 ppb (Mikol et al. 1988).

Table 19-3. Comparison of Maximum Measured Sulfur Dioxide Concentrations by the SRS with Georgia and South Carolina Standards

with Georgia and South Caronna Standards						
			Maximum measured			
Measurement	Georgia and South Carolina		concentration			
Period	standards (µg m <sup>-3</sup> or ppb)		( $\mu g m^{-3} \text{ or ppb}$ )			
3 hours	1300	61				
24 hours	365	6				
Annual	80	3				

A series of tests of the powerhouse emissions were carried out in 1988 and showed all were in compliance. The 291-F stack exceeded the limit for oxides of nitrogen. A deteriorating acid absorption column was reworked, which brought the stack emissions into compliance. An absorber column control project was planned for 1989. Emissions estimates and opacity measurement information is compiled in <a href="Chapter 17">Chapter 17</a> under Coal Ash in the discussion about releases of coal and oxides of nitrogen to air.

## **CONCLUSIONS**

Based on available monitoring data, there is little evidence to suggest that SRS operations have resulted in elevated concentrations of nonradiological contaminants to locations beyond the Site boundary. Although this assertion is supported by a relatively small amount of data, available environmental monitoring information does not support an appreciable source term from the SRS for any nonradiological contaminant. This holds true for all identified chemicals and heavy metals of concern measured in surface water, groundwater, and ambient air. Refer to <a href="Chapter 20">Chapter 20</a> for a more detailed conclusion regarding measured concentrations of mercury and chromium in environmental <a href="media">media</a>.

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